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The Coefficient of Friction of High Polymers as a Function of Pressure

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CONTENTS

ABSTRACT

In a previous paper we described a method for calculating the coefficient of friction μ for thin, solid films deposited on harder substrates. To use this method the shear strength of the film material as a function of pressure must be known. A major limitation of the earlier study was the paucity of such data for materials of interest as dry film lubricants. Recently data have become available for five high polymers: low-density polyethylene, high-density polyethylene, polypropylene, polyvinylidenefluoride, and polytetrafluoroethylene. This report is concerned with the frictional behavior of these same materials in addition to a copolymer of ethylene and tetrafluoroethylene and a copolymer of tetrafluoroethylene and hexafluoropropylene, both in bulk form and as thin films. The experimental values of μ for each polymer agreed well with the values calculated from the pressure/shear strength data, even when this data was extrapolated to higher or lower pressures. It is concluded that μ as a function of pressure can be determined from shear strength measurements, and conversely shear strength as a function of pressure can be estimated from friction measurements of thin films. In general, for thin polymer films, where pressures are usually high, μ will be determined almost entirely by the slope of the shear strength-vs-pressure curve. For bulk polymer specimens μ will be greatly influenced by the intercept on the shear strength axis of that curve and the hardness of the polymer. This accounts for the large difference in the frictional properties between bulk specimens of high-density and low-density polyethylene.

PROBLEM STATUS

This is an interim report on NRL Problem C02-03 and a final report on NRL Problem C02-22, which has been closed.

AUTHORIZATION

THE COEFFICIENT OF FRICTION OF HIGH POLYMERS AS
A FUNCTION OF PRESSURE

INTRODUCTION

As a result of an early investigation Bowers, Clinton, and Zisman (1) proposed that the coefficient of friction μ for solid film lubricants could be approximated by the product of μ for the film material in bulk form and the ratio of the mean yield pressure of the film material to that of the substrate. In deriving this relationship it was noted that its validity depended on the assumption that the shear strength of the film material was essentially independent of pressure. Subsequently, large discrepancies between calculated and experimental values of μ were observed when the hardness (Vickers Hardness Number is proportional to the mean yield pressure) of the substrate was several orders of magnitude greater than the hardness of the film (2). The theory was then modified to include the variation of shear strength with pressure, and equations were developed for calculating μ from material constants of the film and substrate, the system geometry, and the normal load (2). With these equations quantitative agreement was found between theory and experiment for such diverse materials as gold, paraffin, and MoS_2.

A major limitation in these studies was the paucity of data relating shear strength to pressure for materials which were being used or were being considered for use as solid lubricants. To overcome this difficulty a cooperative program was arranged with Dr. L. Towle of the Solid State Division at NRL. He investigated the effects of pressure on the shear strengths of five well-defined, high polymers which we proposed (—low-density polyethylene (LDP), high-density polyethylene (HDP), polypropylene, polyvinylidenefluoride (PVDF), and polytetrafluoroethylene (PTFE). The author has determined the frictional behavior of these same polymers and two additional copolymers—tetrafluoroethylene-hexafluoropropylene and ethylene-tetrafluoroethylene block copolymers—both in bulk form and as thin films on harder substrates. A comparison of these experimental values to those calculated from the shear strength/pressure data form the substance of this report. The investigation of the pressure effects on shear strength will be reported elsewhere (3,4) and will be only briefly described here.

The shear specimens were 1/4-inch-diameter polymer disks, usually 3 to 10 mils thick, which we fabricated from the same materials used to prepare the friction specimens. These were compressed between a single pair of circular anvils at a predetermined pressure P, and the torque M required to produce rotation was measured. The shear strength S at each pressure was determined from

$$S = \frac{3}{2\pi a^3} M, \tag{1}$$

where a is the radius of the anvil. This equation is valid when the pressure is sufficiently high to cause shearing of the entire sample and to prevent any slipping at the anvil/sample interface. If all resistance to motion is defined as friction, a coefficient of friction can also be calculated directly from the measured torque by

$$\mu = \frac{3}{2\pi a^3}\left(\frac{M}{P}\right). \tag{2}$$

Using the above definition, Eq. (2) would then be correct for all conditions regardless of whether the sample slips or is sheared. Equation (2) was used by Boyd and Robertson (5)

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in determining μ at high pressures for a wide variety of lubricants. However, in a discussion published with their paper Bridgman commented, "The data presented, except for two or three substances, lie in the range of pressures in which surface slip has disappeared and the relative motion occurs because of internal slip or shear. Hence, although from the point of view of applications the results are properly described in terms of a 'coefficient of friction,' from the point of view of the mechanism of the yield process, the results might more significantly be described in terms of the shearing strength of the material as a function of pressure." We believe that the latter view is fundamental and that Eq. (2) must be verified by experimental values of friction on thin films.

APPARATUS AND MATERIALS

The friction-measuring apparatus employed was a "stick-slip machine" similar to that described by Goodzeit et al. (6) and previously used by us in numerous investigations (2,7-10). With this device the coefficient of friction is determined between an elastically restrained sphere and a plane surface which is driven at a uniform velocity. The spherical slider is locked in a chuck so that there is no rotation. In these experiments the sliders were 1/2-inch-diameter spheres of either 440C steel or single-crystal sapphire. The driven specimens were either the polymer films deposited on hard substrates or the thick polymer disks. The surfaces of the polymer disks were abraded under water with 600A-grit silicon carbide paper, rinsed in distilled water, and dried in a clean desiccator.

The source, structure, and several physical properties of the high polymers are given in Table 1. The sliders and substrate materials are listed in Table 2. All coefficients of friction were determined at 25°C using a sliding velocity of 0.01 cm/sec.

In this report the coefficient of friction will be discussed as a function of pressure and load. The pressure on each thick disk specimen was assumed to result from the plastic deformation at the areas of real contact and, therefore, was equal to the mean yield pressure of the polymer and essentially independent of load. The pressure on each thin film was considered to result from elastic deformation of the substrate and slider and was calculated from the classical Hertz equation neglecting any contribution of the film, i.e., the film was assumed to deform plastically and have negligible thickness. Also implied is that the real area of contact and the geometric area of contact are equal and that no contact occurs between the slider and substrate. It follows from the discussion by Tabor (11) on the indentation of a plane surface by a harder sphere that the deformation will be elastic if the pressure is less than ca 0.4 of the mean yield pressure of the plane.

Towle (3,4) found that, above some limiting pressure, the shear strength increased almost linearly with pressure for all five polymers. At very low pressures the deviation from linearity could be attributed to the slipping of the sample at the anvil surface. The one exception was polytetrafluoroethylene where a discontinuity occurred at a pressure of 2000 kg/cm^2. The shear curve for each polymer is given in Fig. 1. The solid portion of each line represents the experimental data from the pressure where slipping ceased to the highest pressure at which shear was determined. The dashed portions are extrapolations. The relationship between the shear strength S and the pressure P can, therefore, be expressed by

$$S = kP + c . \tag{3}$$

This is a less complicated relationship than that suggested by Bridgman's data for other solids as reported earlier (2), where S was proportional to some power of P. From Eq. (3) it follows that if, as we have proposed, μ can be expressed as the ratio of S to P, then

$$\mu = S/P = \frac{c}{p} + k . \tag{4}$$

Table 1
The Source, Structure, and Physical Properties of the Polymers

Polymer	Source	Basic Monomer Unit(s)	Density (g/cm^3)	Crystalline Melting Point (°C)	Mean Yield Pressure* (kg/cm^2)
Polyethylene (Low density)	U.S. Industrials Chemical Company	H H $\;\mid\;\mid$ -C-C- $\;\mid\;\mid$ H H	0.915	102	155
Polyethylene (High density)	E.I. du Pont de Nemours and Company	H H $\;\mid\;\mid$ -C-C- $\;\mid\;\mid$ H H	0.959	130.4	690
Polypropylene	Hercules Powder Company	H H $\;\mid\;\mid$ -C-C- $\;\mid\;\mid$ H CH_3	0.901	167	1350
Polyvinylidenefluoride	Pennsalt Chemicals Corp.	H F $\;\mid\;\mid$ -C-C- $\;\mid\;\mid$ H F	1.76	171	1110
Polytetrafluoroethylene	E.I. du Pont de Nemours and Company	F F $\;\mid\;\mid$ -C-C- $\;\mid\;\mid$ F F	2.2	327	400
Ethylene-tetra-fluoroethylene copolymer	E.I. du Pont de Nemours and Company	H H F F $\;\mid\;\mid\;\;\mid\;\mid$ -C-C- -C-C- $\;\mid\;\mid\;\;\mid\;\mid$ H H F F	1.70	270	630
Tetrafluoroethylene-hexafluoropropylene copolymer	E.I. du Pont de Nemours and Company	F F F F $\;\mid\;\mid\;\;\mid\;\mid$ -C-C- -C-C- $\;\mid\;\mid\;\;\mid\;\mid$ F F F CF_3	2.1	290	420

*Determined from Vickers or Knoop hardness measurements made on the polymer disks used.

Table 2
Properties of the Sliders and Substrates

Slider or Substrate	Mean Yield Pressure* $(10^3 \ kg/cm^2)$	Young's Modulus $(10^6 \ kg/cm^2)$
Soda-lime glass	48.8	0.73
Pyrex	49.3	0.63
AISI 304 stainless steel	20.1	2.1
AISI 440C steel	77	2.1
Sapphire	165	3.7

*Determined from Vickers or Knoop hardness measurements made on the substrates used.
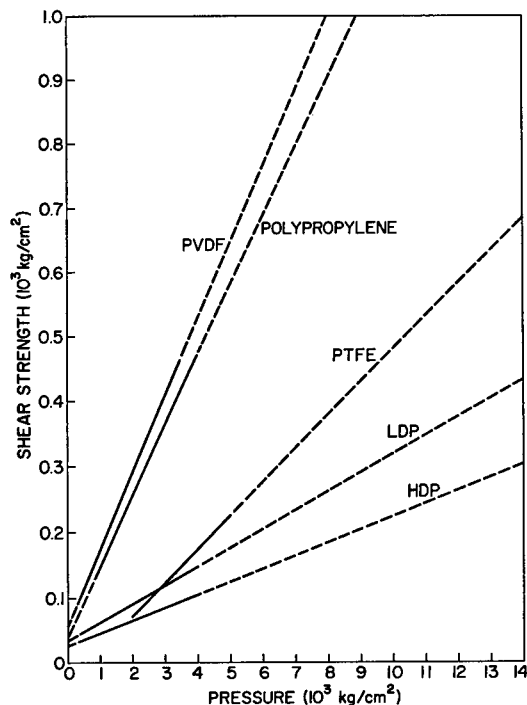
Fig. 1 - The effect of pressure on the shear strengths of polymers

Therefore, if the equation for shear can be extrapolated, μ should decrease with increasing pressure and approach a lower limit equal to k.

RESULTS

Low-Density Polyethylene

The friction specimens were prepared by burnishing the fine powder (average particle size 20 microns) onto acid-cleaned soda-lime glass and Pyrex microslides. This was accomplished by holding the slides against a polishing wheel covered with a nylon cloth charged with the powder. The slides were then placed in an oven at 150°C for 1 hour and then slowly cooled. These films were relatively thick and easily visible. The film deposited on the soda-lime slide was then rubbed with a clean polishing cloth until the film was no longer visible to the unaided eye. A low-density polyethylene (LDP) disk, 1-1/8-inch in diameter and approximately 1/2 inch thick, was molded at 150°C for 15 minutes at 1000 psi and then cooled slowly.

The friction data for LDP are summarized in Table 3. For the initial traverses with a 440C steel slider over the film deposited on Pyrex, the kinetic coefficient of friction μ_k appeared to decrease markedly with increasing pressure. However, on this relatively thick film the large decrease can be explained, in part, as an effect of film thickness. Figure 2 illustrates the manner in which pressure would vary with the load for a film thickness T1. For very small loads the pressure is determined entirely by the yield pressure of the film material (region ab). As the load is increased, the substrate begins to support part of the load and the pressure increases along bc. Beyond point c the load is sufficiently high so that the pressure is essentially determined by the elastic properties of the substrate and slider. With a thinner film, T2, the curve is displaced to the left and point c is reached at a lower load. The pressures given in Table 3 were all determined from the elastic properties of the slider and substrate as represented by the dashed line in Fig. 2. At the lower loads the real pressures correspond to the region bc. Therefore, the reported pressures are greater than the actual value, the error decreasing as the load is increased.

Table 3
The Kinetic Coefficient of Friction for LDP

| Sample	Load (kg)	Pressure (kg/cm^2)	Kinetic Coefficient of Friction for Several Traverse Numbers					
			1st	2nd	5th	10th	15th	20th
Disk	1	155	0.40	0.37	0.37	—	—	—
Film on Pyrex	0.1	1600	0.25	—	—	—	—	—
	0.2	2050	0.15	0.16	0.16	0.18	0.185	—
	0.5	2800	0.13	0.17	0.12	0.08	—	—
	1	3500	0.11	0.12	0.13	0.065	0.06	0.06
	2	4300	0.085	0.09	0.09	0.08	—	—
	5	6000	0.07	0.07	0.065	0.06	—	—
	7.5	6850	0.06	0.06	0.06	0.06	—	—
	10	7500	0.055	0.05	0.05	0.045	—	—
Film on soda-lime glass	0.2	2200	0.06	—	—	—	—	—
	0.5	2950	0.05	—	—	—	—	—
	1	3750	0.05	0.05	0.05	0.05	0.05	0.055
	2	4700	0.045	—	—	—	—	—
	5	6400	0.05	—	—	—	—	—
	7.5	7350	0.05	—	—	—	—	—
	10	8050	0.05	0.05	0.05	0.05	0.055	0.055
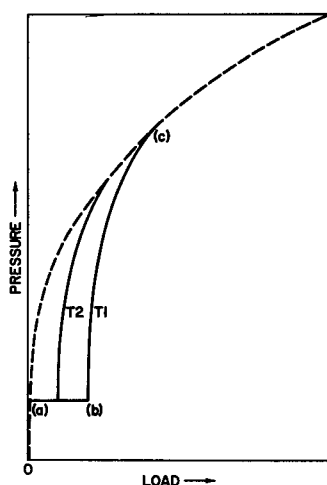
Fig. 2 - The effects of film thickness and load on film pressure

Increasing the load or making multiple unilateral traverses over the same track caused the LDP to be squeezed out of the contact area and effectively decreased the film thickness. Therefore, conditions moved toward the region where film thickness ceases

to have an important effect; i.e., the pressure calculations are more accurate. At low loads μ_k was found to decrease with repeated traverses; at high loads μ_k was low on the first traverse and remained nearly constant.

The film on soda-lime glass was rubbed to remove excess polymer and reduce film thickness prior to the friction measurements. The results indicated that the film was sufficiently thin so that thickness did not significantly influence the calculated pressures. The kinetic coefficient of friction for all conditions was approximately 0.05, the value which was approached on the thicker film by repeated traverses or high loads. For the film on soda-lime glass, the calculated pressures are considered to be accurate. Hence, over the range of pressures from 2000 to 8000 kg/cm^2, there was little change in μ_k. However, on the LDP disk, μ_k was 0.40. The data for the film on soda-lime glass (open circles) and for the polymer disk (solid circle) are summarized in Fig. 3. The pressure coordinate for the polymer disk is the mean yield pressure of the LDP as determined from Vickers Diamond Pyramid Hardness measurements made on the same specimen. The dashed curve, which represents the values of μ as calculated from Fig. 1 and Eq. (4), agrees reasonably well with the experimental values.
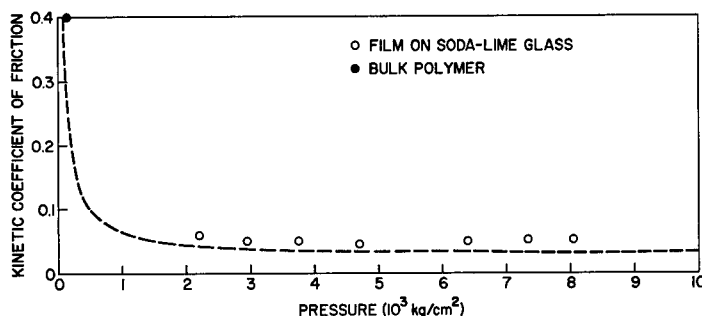

Fig. 3 - The kinetic coefficient of friction of
LDP as a function of pressure

High-Density Polyethylene

Five high-density polyethylene (HDP) films were deposited on soda-lime glass from a solution in xylene at 120°C. The first film was prepared by placing several drops of solution on the preheated glass. The second was formed in a similar manner but followed by a 5-minute immersion in xylene at 115°C. The other three films were prepared by immersing the room-temperature glass in the hot solution for 1 second, 10 seconds, and 10 minutes. The HDP immediately precipitated onto the cooler glass. After a short time, as the temperature of the glass approached the solution temperature, the film began to dissolve. All five films were placed in a vacuum oven at 100°C for 3 hours and then stored in a desiccator. A HDP disk was prepared by heating the pellets in a mold at 160°C for 1-1/2 hours.

Friction measurements were made with a 440C steel slider traversing the five HDP films at loads of 1, 5, and 10 kg (pressures 3750, 6400, and 8050 kg/cm^2). The kinetic coefficient of friction fluctuated during each first traverse, and the average value varied for independent measurements on the same film. However, there was no significant difference in the average value of μ_k among the five films. The average value of μ_k for all films and the range of values obtained for all measurements at each load are given in Fig. 4. Also included is the value of μ_k for the HDP disk (solid circle) plotted at the

Fig. 4 - The kinetic coefficient of
friction of HDP as a function of
pressure
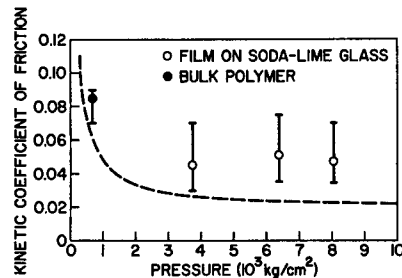
yield pressure of this polymer, 690 kg/cm^2. These values are for the initial traverse.
With repeated traverses on each film, μ_k did not decrease as it did with the thick LDP
film but was nearly constant for several traverses. After a number of traverses, μ_k fre-
quently increased as a result of slider-to-substrate contact through the film. The dashed
line in Fig. 4 indicates the coefficient of friction as calculated from Fig. 1 and Eq. (4).
A sixth film was prepared by rubbing a HDP pellet over the surface of soda-lime glass
which was heated to 135° to 150°C. The resulting film was not visible to the unaided eye,
but its presence was verified by observing the contact angle of a water drop placed on
the surface. With this film, slider-substrate contact frequently occurred and μ_k increased
with repeated traverses. However, at pressures of 2950 and 3750 kg/cm^2 for a first tra-
verse, when there was no apparent substrate damage, μ was 0.07 and 0.06, respectively.

The difference in μ_k between the LDP and HDP disks is striking, 0.40 compared to
0.085. Large differences in friction between these two types of polyethylene have pre-
viously been reported (9). This anomaly can now be better understood by noting the
manner in which the shear strength, and hence μ, vary with pressure. At very low pressures
μ decreases rapidly with increasing pressure. At higher pressures it asymptotically
approaches some lower limit. Therefore, since the pressure on the bulk polymer, over
a wide range of loads, is determined by the mean yield pressure of the polymer, μ is
greater for the softer LDP than for the harder HDP. For thin films subjected to equal
loads, the pressure will be equal for both type polymers and the difference in μ will be
greatly diminished.

Polypropylene

Three polypropylene (PP) films were deposited on soda-lime glass slides from solu-
tion in xylene at 120°C. The first two were prepared by immersing the room-temperature
glass into the solution for 1 second and 1 minute. The third film was formed on a preheated
glass slide by a 10-second immersion. The slides were dried in a vacuum oven at 60°C
for 4 hours and then stored in a grease-free desiccator.

Friction was measured on each film at loads from 0.5 to 10 kg. During each traverse
μ_k remained nearly constant and was reproducible for independent determinations at
each load. There were no significant differences in the frictional properties of the three
films. The values of μ_k for the first traverse at each pressure are plotted in Fig. 5. One
set of five multiple traverses was made on one film at a load of 0.2 kg (pressure 2200
kg/cm^2). The kinetic coefficient of friction on the first traverse varied from 0.165 to
0.20 with an average value of 0.185. This indicates that the film thickness was influencing
friction at this load, and the reported pressure may be too high. At loads of 0.5 kg or
greater, μ_k remained constant with repeated traverses over the same track. This implies
that the thickness of these films had only a minor effect on the calculated pressure and
that polypropylene films were more durable than the HDP films. The solid circle in Fig. 5
represents the kinetic coefficient of friction for a polypropylene disk at a load of 1 kg.
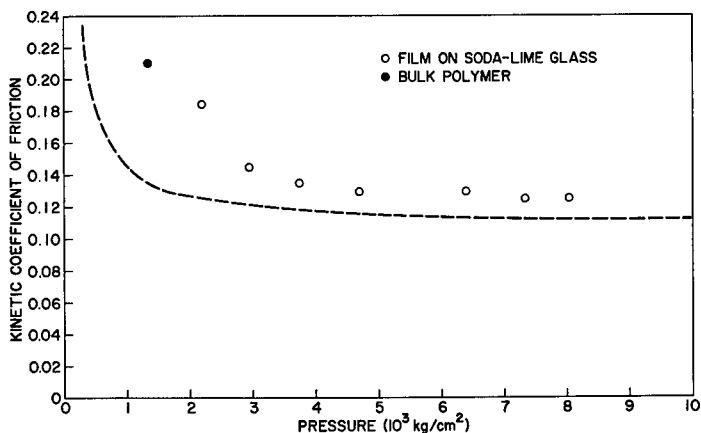Also included, dashed curve, are the calculated values of μ.

Fig. 5 - The kinetic coefficient of friction
of PP as a function of pressure

Polyvinylidenefluoride

Films of polyvinylidenefluoride (PVDF) were prepared from room-temperature solutions in dimethylsulfoxide and in N,N-dimethylformamide by placing several drops of the solution on one of the substrates. Films formed from the former solution peeled away from the substrate during the friction measurements and were unsatisfactory. The results reported here are for the films deposited from N,N-dimethylformamide. PVDF films were deposited on two acid-cleaned Pyrex and two 304 stainless-steel platens. The solvent was allowed to evaporate slowly for 1 day at room temperature and then for 3 days at 165°C. The temperature was then raised above the polymer melting point for 20 minutes. One Pyrex and one steel specimen were quenched in room-temperature water; the remaining two specimens were cooled slowly in the oven. During each initial traverse there was usually little or no variation in μ_k; during a few of these measurements μ_k fluctuated as much as 0.02 from the average value. The kinetic coefficient of friction was independent of the number of traverses over the same track except that, after five to ten traverses, slider-to-substrate contact occasionally occurred. This was accompanied by an increase in friction and by substrate damage. There was no apparent difference between the frictional properties of the quenched and slowly cooled films. Friction measurements for a first traverse with a 440C steel or a Pyrex slider on the quenched films are summarized in Fig. 6. At pressures greater than ca 8000 kg/cm^2, the deformation of the 304 stainless-steel substrate is not entirely elastic; therefore, there is a small error in the calculated pressure above this value.

A PVDF film was deposited on soda-lime glass by permitting the solvent to evaporate at 25°C for 4 days. This was followed by heating at 165°C for 3 days. The values of μ_k at pressures between 2200 and 8000 kg/cm^2 were again within the scatter of the data shown in Fig. 6. Two other films, one on soda-lime glass and one on sapphire, gave results which were not reproducible. They were deposited by solvent evaporation at 25°C for 2 days, heating at 130°C in a vacuum for 8 hours, and heating at 130°C in air for 15 hours.

A "rubbed" film of PVDF was also prepared on soda-lime glass at 135° to 150°C in a similar manner as previously described for HDP. This film was easily visible. Contact occurred between the 440C steel slider and the substrate for all loads greater than 1 kg (pressure 3750 kg/cm^2). At the low loads μ_k decreased with the number of traverses and reached a minimum value before the film broke down. These minimum values are
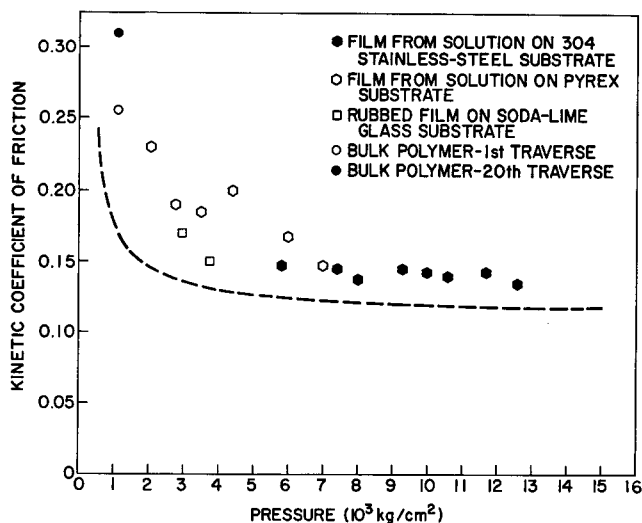
Fig. 6 - The kinetic coefficient of friction of
PVDF as a function of pressure

also included in Fig. 6. With the bulk polymer specimen μ_k increased with repeated
unilateral traverses. Therefore, two values are given in Fig. 6, one for the first traverse
(open circle) and a second for the 20th traverse (closed circle). This effect will be discussed
later. The agreement between the calculated values (dashed line) and the experimental
points is again reasonably good.

Polytetrafluoroethylene

One "rubbed" film of polytetrafluoroethylene (PTFE) was prepared on soda-lime glass
at ca 260°C. This film was easily ruptured so that μ_k increased rapidly after the first
traverse. However, it was possible on some areas of the film to make a single traverse
without causing any substrate damage. Values of μ_k for the first traverse with a 440C
steel slider are given in Fig. 7. Towle's curve of shear vs pressure (4) for PTFE below
2000 kg/cm^2 showed a distinct curvature. At this pressure a discontinuity occurred, and
above 2000 kg/cm^2 the relationship became nearly linear. Below the discontinuity μ_k
would increase with decreasing pressure, as shown in Fig. 7. Of the five polymers for
which the shear strength data are known, PTFE is the only one where the experimental
points fall below the calculated curve. This supports the theory that for PTFE some
shearing occurs at the interface as well as within the polymer (1).

Ethylene-Tetrafluoroethylene Block Copolymer

"Rubbed" films were prepared at 260° to 285°C on soda-lime glass and on 304 stainless
steel and at ca 190°C on soda-lime glass. Visible films formed readily even at the lower
temperature, which is approximately 80°C below the melting point of ethylene-tetrafluoro-
ethylene (ETFE) copolymer. It was possible to make multiple traverses over some areas
of all films without breaking through the film. In general, the average μ_k for the first traverse
was slightly higher than it was for subsequent traverses. After several traverses μ_k
remained constant for as many as 20 traverses. These values of μ_k together with the
values for a thick disk (solid and open circles) are given in Fig. 8. No measurements of
the shear strength as a function of pressure are available for ETFE. However, the values
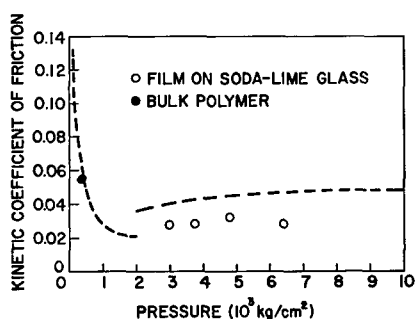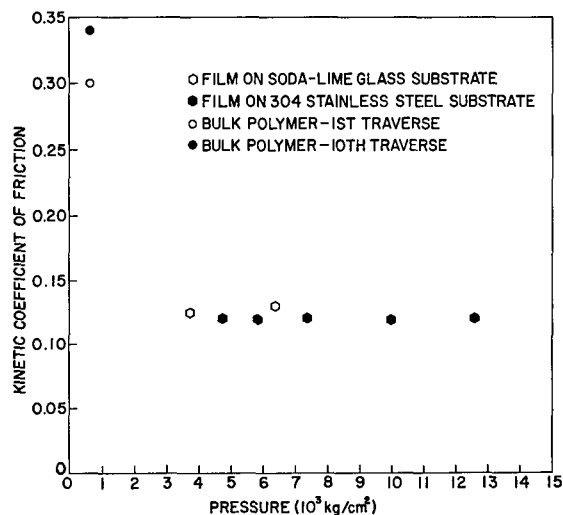
Fig. 7 - The kinetic coefficient of friction of PTFE as a function of pressure

Fig. 8 - The kinetic coefficient of friction of an ETFE copolymer as a function of pressure

of k and c in Eq. (3) can now be estimated from the friction data and Eq. (4). The slope k, from the horizontal asymptote in Fig. 8, is approximately 0.12. The use of this number along with the values of μ and P for the disk specimen (solid circle) and Eq. (4) gives the value of c as 140 kg/cm² to a first approximation.

Tetrafluoroethylene-Hexafluoropropylene Copolymer

Films of tetrafluoroethylene-hexafluoropropylene (FEP) copolymer were prepared by the rubbing technique at ca 260°C on soda-lime glass, 304 stainless steel, and sapphire. The kinetic coefficients of friction for a 440C steel slider traversing the first two films and for a sapphire slider traversing the third film are plotted in Fig. 9. Some substrate damage to the 304 stainless-steel substrate was observed at all pressures. This may explain the slightly higher values of μ_k for this film than those obtained on the glass substrate. However, the fact that there was only a small difference, that there was little or no fluctuation in μ_k during any one traverse, and that μ_k did not change with repeated traverses indicates that any contribution to the total friction force caused by slider-to-substrate adhesion was a secondary effect. As noted earlier, at pressures greater than 8000 kg/cm², the deformation of the 304 stainless steel is not entirely elastic and the calculated pressures are slightly lower than the actual pressures. These data points in Fig. 9 should, therefore, be displaced toward a higher pressure and a lower μ_k. The higher friction for the sapphire substrate cannot readily be explained. Although no substrate damage was observed, it is possible, because of the extreme hardness of sapphire,
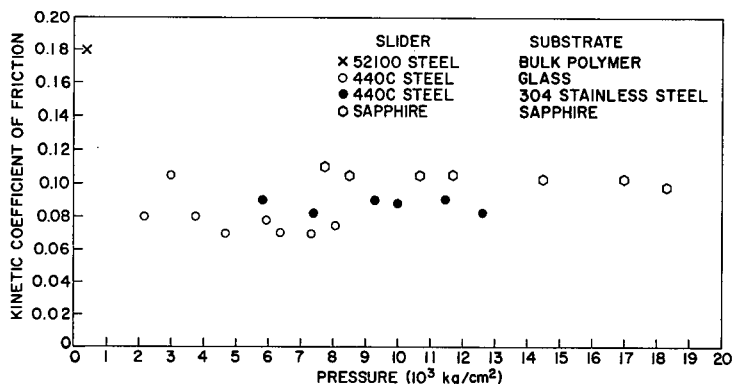
Fig. 9 - The kinetic coefficient of friction of a
FEP copolymer as a function of pressure

that the wear which occurred was too small to be detected. However, there was little or
no variation in μ_k during any traverse, and μ_k remained constant and reproducible with
repeated traverses. Estimates of the values of k and c for Eq. (3) as determined from
the friction data are 0.07 and 45 kg/cm^2.

Polymer Disks

The sliders used for the friction measurements were 440C and/or 52100 steel. For
the several polymers where both sliders were used, no significant difference could be
attributed to the type of slider. In general the load, in the range 0.5 to 10 kg, had only a
minor effect on μ_k, but the static coefficient of friction μ_s tended to decrease as the load
was increased. The kinetic coefficient of friction was nearly constant during any one
traverse, and for most polymers μ_k did not change appreciably with repeated traverses.
The most notable exception was PVDF. As illustrated in Fig. 10, μ_k increased with repeated
traverses, after the first traverse, before reaching a constant value. The same trend
was also observed with ETFE but to a lesser degree. A more typical result was that of
PP (Fig. 10). The static coefficient of friction decreased markedly on the second traverse
with all polymers (Fig. 10). After the second traverse μ_s increased with PVDF but
remained nearly constant with the other polymers.

DISCUSSION

In comparing the values of μ_k obtained experimentally to those values calculated from
the shear strengths, several variables which could result in discrepancies will be discussed.

The shear strength of the polymers may depend on the rate at which they are sheared.
The angular speed was approximately 30° per sec in the shear measurements (3) on a
1/4-inch-diameter sample the sliding velocity would vary from zero at the center to 0.17
cm/sec at the circumference or have an average value of 0.11 cm/sec. The sliding
velocity in the friction experiments, 0.01 cm/sec, was an order of magnitude smaller.
However, Towle (3) found that a fivefold increase in the rotational rate produced little or
no change in torque. Therefore, the difference in sliding velocity probably caused at most
only a minor variation. The sliding velocity is also sufficiently low so that frictional
heating can be ignored.

A second factor is the effect of film thickness. It has been assumed that the film
thickness was negligible but that no contact occurred through the film. This is an idealized
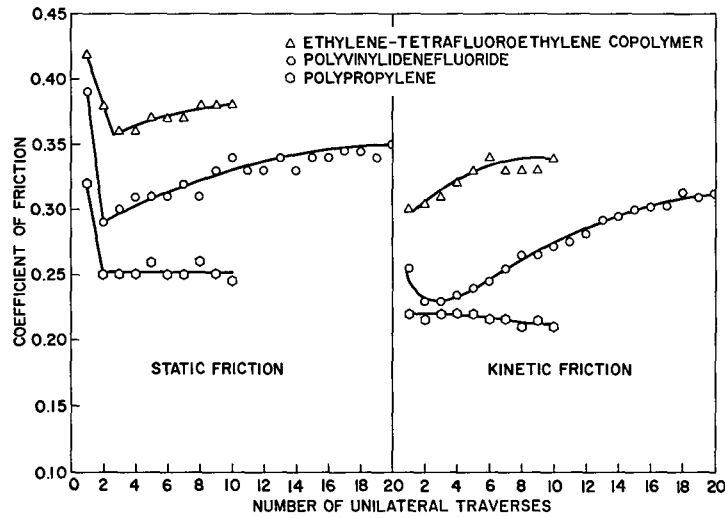
Fig. 10 - The effect of multiple traverses on the static
and kinetic coefficients of friction of several polymers

condition. Any contribution of the film in supporting the load would result in a decrease
in pressure, although the much greater hardness of the substrate diminishes this effect.
Since μ_k increases with decreasing pressure, any contribution of the film in supporting
the load would cause the experimental values of μ_k to be greater than the calculated
values. Any contact between the slider and substrate would produce the same result. The
effect of film thickness was minimized by using multiple traverses to decrease the thick-
ness (after one traverse the film was frequently no longer visible) and by examining the
tracks on the substrate for evidence of wear using a light microscope at 75X. Measure-
ments obtained on any areas of the film where substrate damage could be detected were
discarded.

Another consideration is the effect of work hardening of the polymers. Towle found
that the shear strength of the polymers increased during the first few rotational cycles
before reaching a constant value. The greatest change was with PVDF (3). The torque
readings he reported were for the steady-state or work-hardened condition. This should
correspond closely to the condition of the thin films or disks after multiple traverses in
the friction experiments.

The coefficient of friction has been assumed to result entirely from shearing the
polymer. In addition, there is a component of friction caused by the plowing of the slider
and the resulting plastic displacement of the polymer. A first approximation of the plowing
force F_p for the thick disks (12) can be estimated from

$$F_p = \frac{d^3 P_m}{12 r_1},\qquad (5)$$

where P_m is the mean yield pressure of the polymer, r_1 is the radius of curvature of the
slider, and d is the track width.

If the area of contact is a circle with a diameter equal to the track width and if the
polymer disks are plastically deformed, then

$$A = \frac{\pi d^2}{4} = \frac{L}{P_m}.\qquad (6)$$

From Eqs. (5) and (6):

$$F_p = \frac{0.12}{r_1}\left(\frac{L^3}{P_m}\right)^{1/2}. \tag{7}$$

That part of the coefficient of friction which is due to plowing μ_p is

$$\mu_p = \frac{F_p}{L} = \frac{0.12}{r_1}\left(\frac{L}{P_m}\right)^{1/2}. \tag{8}$$

At a load of 1 kg, μ_p is approximately 0.015 for the softest polymer and 0.005 for the hardest. This plowing effect would be much less for the thin films, since the deformation would be greatly diminished.

It is of particular interest to consider the pressure/shear strength relationship as applied to friction of bulk polymers. If very light loads are excluded, the pressures at the real areas of contact (the asperities) will be independent of the applied load and equal to the mean yield pressure of the polymer. This pressure, for the polymers studied, occurs in the region where μ is decreasing rapidly with pressure (see Figs. 3 through 7). The harder of two polymers having similar shear strength-vs-pressure curves would have the lower μ when measured as a thick specimen, but the same μ when measured as a thin film under comparable conditions. In general, for thin polymer films, where the pressures are usually high, μ will be determined almost entirely by the slope of the shear strength-vs-pressure curve. For bulk polymers μ will be greatly influenced by the intercept of the curve and the hardness of the polymers.

The effects of temperature and sliding velocity were not investigated. An increase in ambient temperature would be expected to cause a decrease in friction since the strength of the film material would diminish and the pressure, determined primarily by the harder substrate, would not decrease proportionally. High sliding velocities would produce the same effect as a result of frictional heating. At very low sliding velocities (low shear rates), it would be predicted that the shear strength, and hence μ, would be greater. This may explain, in part, the higher values of μ_s compared to μ_k.

In this study no concerted effort was made to establish the film durability or to develop methods of film preparation for optimum wear life. Considered only from the standpoint of low friction, the most promising materials for thin-film lubricants are LDP, HDP, and PTFE.

SUMMARY AND CONCLUSIONS

Coefficients of friction for thin films of seven interesting and well-defined high polymers deposited on several hard substrates have been measured for loads between 0.2 and 10 kg (maximum pressure 18,300 kg/cm^2, sapphire substrate). The experimental values of μ_k agreed well with the values calculated from the pressure/shear strength data even when these data were extrapolated to higher pressures. The coefficient of friction was also determined for thick disks of the same polymers. An explanation has been given to account for the large difference in friction between bulk high-density and low-density polyethylene.

It is concluded that μ as a function of pressure can be determined from shear strength/pressure measurements and conversely shear strength as a function of pressure can be calculated from friction measurements of thin films on harder substrates.

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13. ABSTRACT

In a previous paper we described a method for calculating the coefficient of friction μ for thin, solid films deposited on harder substrates. To use this method the shear strength of the film material as a function of pressure must be known. A major limitation of the earlier study was the paucity of such data for materials of interest as dry film lubricants. Recently data have become available for five high polymers: low-density polyethylene, high-density polyethylene, polypropylene, polyvinylidenefluoride, and polytetrafluoroethylene. This report is concerned with the frictional behavior of these same materials in addition to a copolymer of ethylene and tetrafluoroethylene and a copolymer of tetrafluoroethylene and hexafluoropropylene, both in bulk form and as thin films. The experimental values of μ for each polymer agreed well with the values calculated from the pressure/shear strength data, even when this data was extrapolated to higher or lower pressures. It is concluded that μ as a function of pressure can be determined from shear strength measurements, and conversely shear strength as a function of pressure can be estimated from friction measurements of thin films. In general, for thin polymer films, where pressures are usually high, μ will be determined almost entirely by the slope of the shear strength-vs-pressure curve. For bulk polymer specimens μ will be greatly influenced by the intercept on the shear strength axis of that curve and the hardness of the polymer. This accounts for the large difference in the frictional properties between bulk specimens of high-density and low-density polyethylene.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Solid film lubricants						
Low-density polyethylene						
High-density polyethylene						
Polypropylene						
Polyvinylidene fluoride						
Polytetrafluoroethylene						
Ethylene-tetrafluoroethylene						
Tetrafluoroethylene-hexafluoropropylene						
Coefficient of friction						